



## Coupling of Photocatalysis and Biological Treatment for Phenol Degradation: Application of Factorial Design Methodology

Hamida Hamdi, Abdelkader Namane, Dalila Hank, Amina Hellal\*

Laboratoire des Sciences et Techniques de l'Environnement, Ecole Nationale Polytechnique, 10 Avenue Hacen Badi, BP182  
El Harrach, 16200 Algiers, Algeria.

Received 26 Jun 2016,  
Revised 07 Dec 2016,  
Accepted 14 Dec 2016

### Keywords

- ✓ Phenol,
- ✓ Degradation,
- ✓ Photocatalysis,
- ✓ Biodegradation,
- ✓ Coupling.

A. Hellal  
[amina.hellal@g.enp.edu.dz](mailto:amina.hellal@g.enp.edu.dz)  
(+213) 23 82 85 35

### Abstract

In this study, the first part was focused on the photodegradation of phenol. The second part concerned a comparison between photocatalytic, biological, and biophotocatalytic treatments. A full factorial experimental design methodology was used to evaluate the effects of phenol concentration,  $\text{TiO}_2$  concentration and pH on phenol photodegradation. The mathematical model employed for  $2^3$  factorial design with interaction verifies the good correlation between the observed and the predicted response values with  $R^2$  and  $R^2_{\text{adj}}$  of 99.77% and 98.97% respectively. Furthermore the model provides the excellent relationship between the independent variables (factors) and the response. Under the optimal conditions values obtained by the factorial experimental design methodology (phenol concentration 20 mg/L,  $\text{TiO}_2$  concentration 2 g/L and pH 9), the predicted percentage of degradation was 64.09%. The combined photocatalytic-biological treatment significantly reduced the degradation time of phenol. Thus, a complete phenol biodegradation of 100 mg/L occurs in 15 hours when using a photocatalytic as a pre-treatment, whereas the biodegradation alone required 47 hours.

## 1. Introduction

The development in agriculture, energy sources, and chemical industries is necessary in order to fulfill the needs and demands of the overgrowing human population. Almost all processes employed by man for the production of goods and services lead to the production of environmental pollutants [1-3]. Some of these pollutants are biologically recalcitrant and inhibitory organics, which greatly reduces microorganism ability to biodegrade the compounds during treatment or in nature [4-6]

$\text{TiO}_2$  heterogeneous photocatalysis process has gained wide attention due to its effectiveness in degrading and mineralizing the recalcitrant organic compounds [7-9]. These allow compounds with complex structures to be transformed into more biologically degradable and less toxic substances [8,10].

The rate and efficiency of a photocatalytic reaction depend on a number of factors which govern the kinetics of photocatalysis. Among these parameters that could be cited: initial concentration of pollutant, mass of catalyst, pH, volume of solution, radiant flux and agitation [11,12].

In recent years, the coupling between the heterogeneous photocatalytic and biological systems for the treatment of different polluted effluents has been proposed recurrently and the success relies on reaching an acceptable biodegradability with the shortest photocatalytic degradation (optimal treatment) and subsequently applying biological degradation, which turns the overall process cheaper and more attractive option [13,14].

The first aim of the present work is to optimize the operational conditions of the photoreactor, and to test the activity of a commercial photocatalyst, whereas the second aim is to compare between photocatalytic, biological and combined photocatalytic-biological treatments.

## 2. Materials and Methods

### 2.1. Chemicals

A commercial photocatalyst titanium (IV) oxide ( $\text{TiO}_2$ ) was obtained from Biochem Chemopharma, Quebec (99.5 % purity). Its molecular weight is 79.87 g/mol.

Phenol purchased from Merck Chemicals was used for all the photodegradation and biodegradation studies.

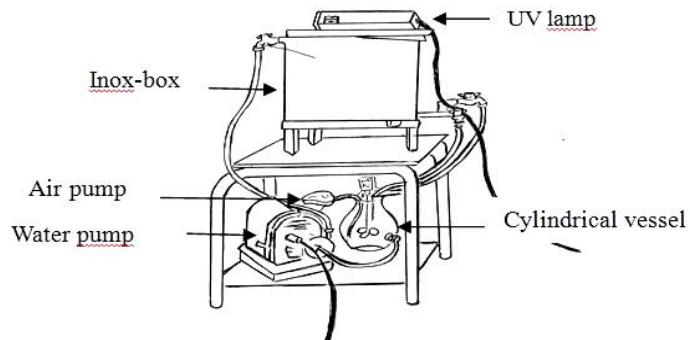
### 2.2. Biological material

The strain used in the present study is *Pseudomonas aeruginosa* ATCC27853, provided by Pasteur institute of Algiers. The growth medium (GM) of the strain consisted of (g/L) peptone 10.0, beef extract 3.0, NaCl 5.0, at the pH value 7.0, autoclaved at 121°C for 15 min.

A minimal culture medium (MM) contained the necessary nutrients for the growth of microorganisms. Its composition (g/L) is:  $\text{KH}_2\text{PO}_4$  1.5,  $\text{K}_2\text{HPO}_4$  0.5, NaCl 0.5,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  0.5,  $\text{NH}_4 \text{NO}_3$  3.0,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  0.02,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  0.02.

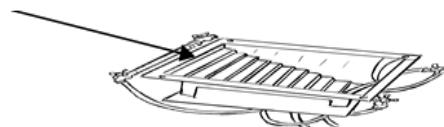
### 2.3. Photoreactor

Photocatalytic degradation experiments are carried out in a photochemical reactor as schematically shown in Figure 1. The photoreactor is composed of two compartments. The first one is a cylindrical vessel containing an aqueous dispersion, which was mixed to ensure uniform mixing. The cylindrical vessel is covered with aluminum foil to reflect irradiation exerting the outer of the vessel. An air pump is used to provide oxygen in order to maintain an aerobic condition inside the vessel. The second compartment, where the photocatalytic reaction occurs, is an inox-box which contains stairs (Figure 2) on the inside to increase surface contact. UV irradiation is provided by a UV lamp (VILBER LOURMAT, FRANCE) which is placed in the middle of the box-cover. The UV lamp emits at a wavelength of 365 nm.



**Figure 1.** Schematic diagram of the experimental setup.

The inside of the inox-box



**Figure 2.** The inside of the photoreactor.

Prior to irradiation, the dispersions were stirred in the dark for 30 min to the establishment of adsorption/desorption equilibrium [15,16], and pH of the solution was beforehand adjusted by adding chlorhydric acid (HCl, 1N) or sodium hydroxide (NaOH, 1N).

### 2.4. Photocatalytic degradation

Phenol degradation tests were carried out in the photoreactor in order to optimize the different factors that affect this process using the factorial design. The photoreactor was filled with 3 L of an aqueous solution of phenol and  $\text{TiO}_2$  at the desired concentrations. Samples taken at different times of irradiation were filtered through 0.45  $\mu\text{m}$

Millipore disks to remove TiO<sub>2</sub> particles before analysis [17,18]. Control experiments with no photocatalyst and in the absence of illumination were performed, showing no significant phenol degradation or loss during the periods of the used time.

### 2.5. Factorial design methodology

In order to optimize the experimental conditions for the photodegradation of phenol, a factorial design with three factors at two distinct levels was performed. Table 1 presents the independent variables and the used levels.

**Table 1.**The levels and the range of variables in photodegradation experiment design.

<b>Independent variables</b>	<b>Coded variable level</b>		
	<b>Low (-1)</b>	<b>Center (0)</b>	<b>High (+1)</b>
Phenol concentration (mg/L) (X <sub>1</sub> )	20	60	100
TiO <sub>2</sub> concentration (mg/L) (X <sub>2</sub> )	400	1200	2000
pH (X <sub>3</sub> )	2.6	5.8	9

### 2.6. Biodegradation tests

Phenol degradation tests were performed in a batch bioreactor at 37°C under aerobic conditions with free cells of *Pseudomonas aeruginosa* ATCC27853.

### 2.7. Coupling of photocatalysis and biological treatment

To investigate the efficiency of the coupling of photocatalysis and biological treatment, different times (4 h, 6 h, and 8 h) of photocatalytic phenol degradation were considered before the biological treatment. The used procedure for coupling of photocatalysis and biological treatment was as follows:

- After different periods of photodegradation, solution was transferred to 2 L flasks for biological treatment
- Appropriate nutrient medium (mentioned above) was added to the flasks
- The inoculum of *P. aeruginosa* was added to the solution
- Sampling at different time intervals was measured regularly.

### 2.8. Analyses

Phenol was quantified by a colorimetric method based on its condensation with 4-aminoantipyrine in the presence of an oxidizing agent, potassium ferricyanide, in an alkaline medium to give a red complex [19]. The absorbance was determined by a spectrophotometer (Shimadzu 1601) at a 510 nm wavelength.

## 3. Results and discussion

### 3.1. Factorial design methodology

The design matrix of coded values for factors and the response Y, measured in each factorial experiment is shown in Table 2. The response, Y, represents the phenol degradation percentage.

**Table 2.** Experimental values for the phenol degradation percentage.

<b>Experiment number</b>	<b>X<sub>1</sub></b>	<b>X<sub>2</sub></b>	<b>X<sub>3</sub></b>	<b>Response (Y)</b>
1	-1	-1	-1	30.61
2	+1	-1	-1	14.1
3	-1	+1	-1	0
4	+1	+1	-1	17.56
5	-1	-1	+1	55
6	+1	-1	+1	1.78
7	-1	+1	+1	64.56
8	+1	+1	+1	32.95
9	0	0	0	24.72
10	0	0	0	24.72

The codified mathematical model employed for  $2^3$  factorial designs with interaction [20,21] was represented as follows:

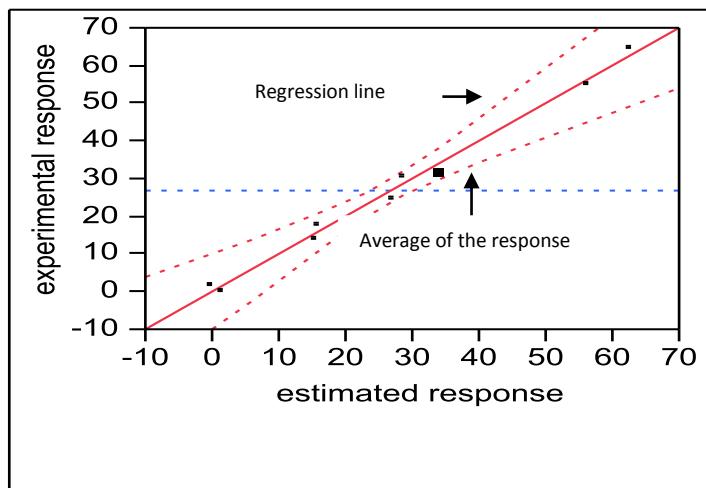
$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_{12} X_1 X_2 + a_{13} X_1 X_3 + a_{23} X_2 X_3 + a_{123} X_1 X_2 X_3 \quad (1)$$

In Eq.(1), Y is the estimated response which represents the % of phenol degradation,  $a_0$  is the independent coefficient (a constant term),  $a_i$  ( $i=1,2,3$ ) are the linear coefficients for the variables, phenol concentration,  $TiO_2$  concentration, and pH respectively,  $a_{ij}$  represents the coefficients of the interaction parameters  $X_i$  and  $X_j$  with  $i < j$ . The coefficients  $a_i$ ,  $a_{ij}$ ,  $a_{ijk}$  were determined by using JMP® 8 software [21,22].

Substituting the coefficient  $a_i$ ,  $a_{ij}$ ,  $a_{ijk}$  in the equation by their values (Table 4), the mathematical model selected will be the following:

$$Y = 26.6 - 10.4725 X_1 + 1.6975 X_2 + 11.5025 X_3 + 6.96 X_1 X_2 - 10.735 X_1 X_3 + 8.485 X_2 X_3 - 1.5575 X_1 X_2 X_3 \quad (2)$$

Figure 3 shows the predicted values versus the experimental values of the percentage of degradation of phenol. The high values of  $R^2 = 99.77\%$  and  $R^2$  adjusted = 98.97% indicate that the model was successful in correlating the response to the studied parameters so a good predictability of the model [23,24].



**Figure 3.** Comparison of the experimental and the estimated response at variable's levels.

### 3.2. The Student's t-test

The Student's 't' test was used to determine the significance of the regression coefficients of the parameters [20].

**Table 3.** Estimated regression coefficients for the phenol degradation percentage.

Parameters	Estimate	Standard error	t-value	p-value
Constant ( $a_0$ )	26.6	0.970265	27.42	0.0001*
Phenol ( $a_1$ )	-10.4725	1.08479	-9.65	0.0024*
$TiO_2$ ( $a_2$ )	1.6975	1.08479	1.56	0.2156
pH ( $a_3$ )	11.5025	1.08479	10.6	0.0018*
Phenol- $TiO_2$ ( $a_{12}$ )	6.96	1.08479	6.42	0.0077*
Phenol-pH ( $a_{13}$ )	-10.735	1.08479	-9.9	0.0022*
$TiO_2$ -pH ( $a_{23}$ )	8.485	1.08479	7.82	0.0044*
Phenol- $TiO_2$ -pH ( $a_{123}$ )	-1.5575	0.743135	-2.10	0.1711

(\*p-value < 0.05)

The Student's *t*-test and P-value were used to determine the significance of the regression coefficients of the parameters. More significant the terms of coefficient if the value of '*t*' is larger and value of '*P*' is smaller (<0.05). The final models in terms of coded parameters after excluding the insignificant terms (as indicated in Table 3) is given in Eq. 3:

$$Y=26.6 - 10.4725 X_1 + 11.5025 X_3 + 6.96 X_1X_2 - 10.735 X_1X_3 + 8.485 X_2X_3 \quad (3)$$

This function describes how the experimental variables and their interactions influence the percentage of degradation of phenol [11, 25]. The positive value of the main effect indicates an increase of percentage phenol degradation in going from the low to the high level of the factor.

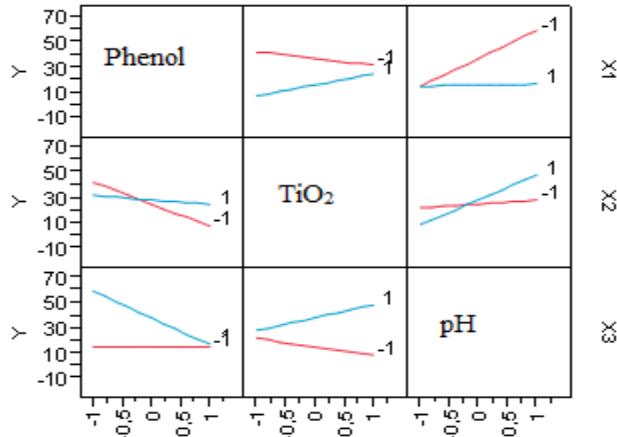
As shown in Table 3, the phenol concentration and pH medium have a negative and a positive effect, respectively. It means that the photocatalytic reaction would be thus favored at a low initial concentration of phenol and high pH medium.

The  $TiO_2$  concentration has no effect on the response but has a significant interaction effect with the initial phenol concentration and the pH medium.

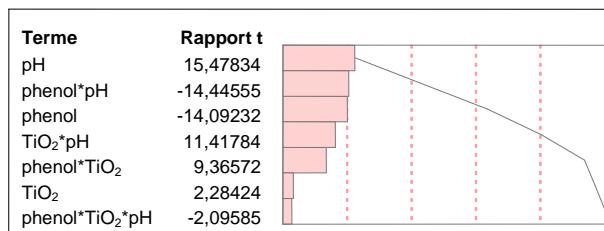
### 3.3. Interaction plots

An interaction (Figure 4) is effective when the change in the response from low to high levels of a factor is dependent on the level of a second factor, i.e. when the lines do not run parallel [25]. Figure 5 shows the significant interactions between the parameters (phenol concentration and pH,  $TiO_2$  concentration and pH, phenol concentration and  $TiO_2$  concentration).

The interaction plots were also generated with ANOVA. All the interactions of the factors were statistically significant in determining % phenol degradation. These plots clearly indicated that interaction between phenol concentration and pH ( $X_1X_3$ ) was stronger than between  $TiO_2$  concentration and pH ( $X_2X_3$ ). The interaction between phenol concentration and  $TiO_2$  concentration ( $X_1X_2$ ) was statistically significant but much smaller.



**Figure 4.** Interaction plot for the phenol degradation percentage.



**Figure 5.** Pareto chart of the standardized effects

### 3.4. Analysis of variance (ANOVA)

In order to establish a correlation between the model prediction and the experimental response, analysis of variance (ANOVA) was used to test the goodness of fit for the polynomial coefficients of the response Y [26].

F-value is a statistically valid measure of how well the factors describe the variation of the data about the mean.

Analysis of variance (ANOVA), indicated in Table 4, demonstrates that the regression model was highly significant. The F-value obtained (59.5972) was higher than the tabular value ( $F_{0.05,5,4} = 6.26$ ) and indicates a good adherence of the model to the experimental results at 95% confidence level.

**Table 4.** Analysis of variance (ANOVA)

Source	Sum of Squares	DF	Mean square	F-value
Model	3821.2625	5	764.253	59.5972
Residual (error)	51.2945	4	12.824	
Correlation total	3872.5570	9		

### 3.5. Estimation of optimal design conditions by the method of desirability function

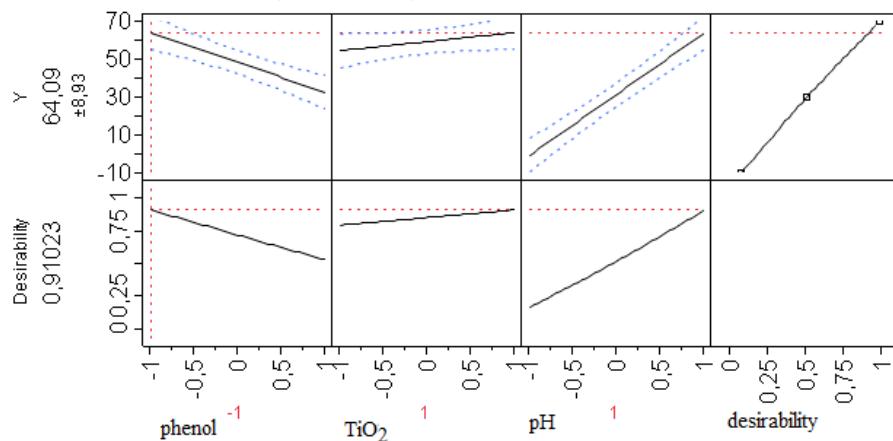
The method of desirability function was used to obtain the maximum of % phenol degradation. The optimum conditions, i.e. the best combination of factor settings for achieving the optimum response was found to be: phenol concentration 20 mg/L,  $TiO_2$  concentration 2000 mg/L and pH 9 for a predicted response of 64.09% with a desirability value of 0.91023 (Figure 6).

These results are found to be in good accordance with those obtained from the surface plot (Figure 7). The surface plot is a useful approach in terms of optimization of the response. Figure 7 shows that with the decrease in initial phenol concentration, the percentage of degradation of phenol increases with a high pH. The Optimum region is attained at the high level of pH and low level of phenol concentration.

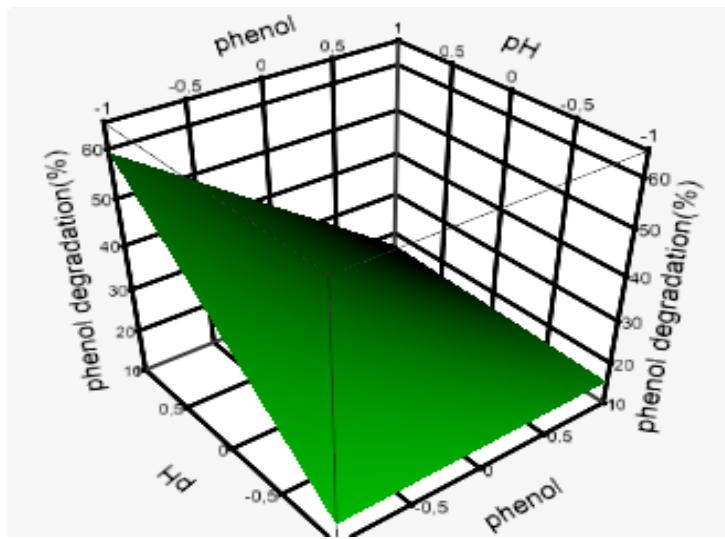
The effect of pH is a complex issue closely related to the properties of the substrate in question and the amphoteric behavior of  $TiO_2$ . The highest efficiency in our study was observed at pH 9. Similar observations have been made by other researchers for phenol and several other types of pollutants [15,27,28].

The highest efficiency of degradation in alkaline pH could be attributed to the more efficient generation of hydroxyl radicals by  $TiO_2$  with increasing concentration of hydroxide ion [27].

According to the literature reports [27,28,29], the degradation rates of phenol and other types of pollutants in the presence of  $TiO_2$  increase with the increase in catalyst concentration up to 2 g/L and a further increase in catalyst concentration leads to a decrease in degradation rates. The optimum of catalyst concentration is 2 g/L which is agreed with our result obtained from the factorial experimental design. At high  $TiO_2$  concentration, particles aggregate which in turn reduces the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface decreased. The increase in opacity and light scattering by the particle may be the other reasons for the decrease in the degradation rate at higher catalyst concentration [30,29].



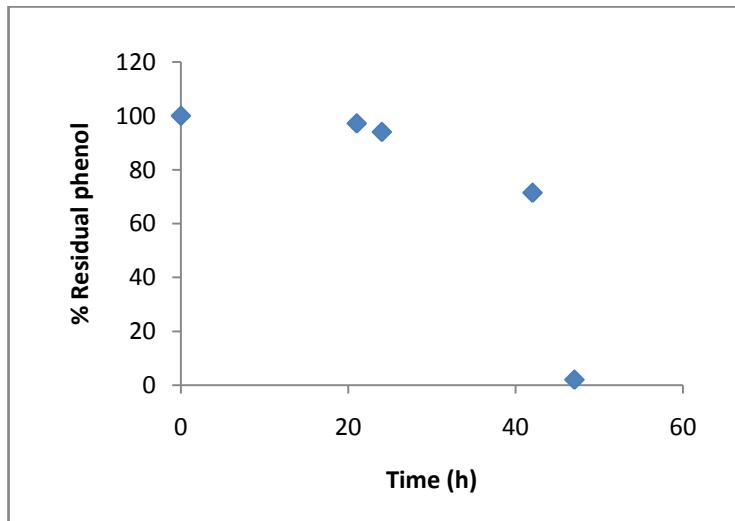
**Figure 6.** Desirability functions for the optimization of the response



**Figure 7.** Response surface plot showing the effect of phenol concentration and pH on phenol degradation percentage.

### 3.6. Biodegradation

Figure 8 shows the results achieved in terms of % of residual phenol; 100 mg/L of phenol were degraded by *P. aeruginosa* at 37°C in aerobic conditions. It can be observed that the time of a complete biodegradation was 47 hours. The same result was found by Ali et al [31].



**Figure 8.** Phenol biodegradation

### 3.7. Coupling of photocatalysis and biological treatment

Table 5 indicates the value of the time and the percentage of phenol degradation by photocatalysis and biological treatment.

**Table 5.** Photocatalytic and biological treatments

	% of phenol degradation (%)	Treatment time (h)
Photocatalytic treatment alone	32	24
Biological treatment alone	100	47

In 24 hours, 32% of phenol was degraded with a photocatalytic treatment alone, and a complete degradation was reached in 47 hours by the biological treatment alone. The table 6 presents the coupling of photocatalytic and biological treatments. The percentage of phenol degradation with biological treatment in combined process was determined after different periods of photodegradation (4, 6 and 8 hours).

**Table 6.** Coupling of photocatalytic and biological treatments

Photocatalytic pre-treatment time (h)	% of phenol degradation after the pre-treatment (%)	Complete biodegradation time (h) after photocatalytic pre-treatment
4	0.5	24
6	1.1	18
8	14	15

The coupling of the two processes was found to be effective in treating phenol. An initial phenol concentration of 100 mg/L required 15 h for complete biodegradation after 8h of photocatalytic pre-treatment.

## Conclusion

The efficiency of photocatalytic degradation of phenol by using the commercial Titanium (IV) oxide ( $TiO_2$ ) as a catalyst in aqueous solution was studied.

The findings suggested that various operating parameters such as initial concentration, catalyst amount and initial pH of the reaction medium can significantly influence the photocatalytic degradation rate of phenol.

This study showed that factorial experimental design approach is an excellent tool and could successfully be used to develop the empirical equation for the prediction and understanding of phenol photocatalytic degradation efficiency and also for determination of optimum conditions maximizing the phenol removal.

As observed from the empirical equation, the initial pH of the solution had the greatest effect on the phenol degradation percentage, followed by phenol concentration-pH interaction, phenol concentration,  $TiO_2$  concentration-pH interaction, and phenol concentration- $TiO_2$  concentration interaction respectively.

The best operational values obtained by factorial experimental design methodology were 20 mg/L phenol concentration, 2 g/L  $TiO_2$  concentration at pH 9. In these conditions, phenol percent removal was 64.09%, achieved after 24 h of irradiation.

The coupling of two processes (photocatalysis and biodegradation) was found to be effective in treating phenol. An initial phenol concentration of 100 mg/L required 15 h of biological treatment for complete mineralization when treated with combination process, whereas the treatment went on up to 47 h when biodegradation alone was employed, and non-complete degradation with only the photocatalysis process (32% of phenol was degraded in 24 h).

## References

1. Zhang Y., Liu H., Shi W., Pu X., Zhang H., Rittmann B.E., *Biodegradation*, 21 (2010) 881-887.
2. Pulgarin C., Invernizzi M., Parra S., Sarri'a V., Polania R., Peringer P., *Catal. Today*, 54 (1999) 341-352.
3. Hazrat A., *Water Air Soil Pollut.*, 213(2010) 251-273.
4. Zhang L., Xua C., Chena Z., Li X., Li P., *J. Hazard. Mater.*, 173 (2010) 168-172
5. Fenoll J., Martínez-Menchón M., Navarro G., Vela N., Navarro S., *Chemosphere*, 91 (2013) 571-578.
6. Daghhrir R., Drogui P., Robert D., *J. Photochem. Photobio. A: Chem.*, 238 (2012) 41-52.
7. Tantis I., Bousiakou L.G., Lianos P., Kalkani H., *J. Mater. Environ. Sci.*, 8 (2017) 1-6.
8. Celin S. M., Pandit M., Kapoor J.C., Sharma R.K., *Chemosphere*, 53 (2003) 63-69.
9. Al-Muhtaseb A.H., Khraisheh M., *J. Water Process Eng.*, 8 (2015) 82-90.
10. Choquette-Labbé M., Shewa W.A., Lalman J.A., Shanmugam S.R., *Water*, 6 (2014) 1785-1806.
11. Salhi A., Aarfane A., Tahiri S., Khamliche L., Bensitel M., Bentiss F., El Krati M., *Mediterr. J. Chem.* 4 (2015) 59-67.

12. Kashif N., Ouyang F., *J. Environ. Sci.*, 21 (2009) 527-533.
13. Sousa M.A., Gonçalves C., VilarVítor J.P., Boaventura Rui A.R., Alpendurada M.F., *Chem. Eng. J.*, 198 (2012) 301-309.
14. Yahiat S., Fourcade F., Brosillon S., Amrane A., *Int. Biodeterior. Biodegr.*, 65 (2011) 997-1003.
15. LinY.X., Ferronato C., Deng N.S., Chovelon J.M., *Appl.Catal. B: Environ.*, 104 (2011) 353-360.
16. Sahoo C., Gupta A.K., *J. Hazard. Mater.*, 215 (2012) 302-310.
17. Ahmed O., Pons M., Lachheb H., Houas A., Zahraa O., *Sustainable Environ. Res.*, 24 (2014) 381-387.
18. Lucas Vaz J.L., Boussaoud A., Ait Ichou Y., Petit-Ramel M., *Analysis*, 26 (1998) 83-87.
19. Liu Q.S., Zheng T., Wang P., Jiang J.P., Li N., *Chem. Eng. J.*, 157 (2010) 348-356.
20. Goupy J., Creighton L., *Introduction aux plans d'expériences*, Dunod (2006).
21. Tinsson W., *plans d'expérience: constructions et analyse statistiques*, Springer (2010).
22. Proust M., *JMP® 8 Introductory Guide*, Second Edition. Cary, NC: SAS Institute Inc (2009).
23. Sakkas V.A., Islam M.A., Stalikas C., Albanis T.A., *J. Hazard Mater.*, 175 (2010) 33-44.
24. Juretic D., Kusic H., Koprivanac N., Bozic A.L., *Water Res.*, 46 (2012) 3074-3084.
25. Bingol D., Tekin N., Alkan M., *Appl. Clay Sci.*, 50 (2010) 315-321.
26. Ayodele O.B., Lim J.K., Hameed B.H., *Chem. Eng. J.*, 197 (2012) 181-192.
27. Abu Tariq M., Faisal M., Saquib M., Muneer M., *Dyes Pigments* 76 (2008) 358-365.
28. Saratale R.G., Noh H.S., Song J.Y., Kim D.S., *J. Environ. Sci Health A Tox. Hazard. Subst. Environ. Eng.*, 49 (2014) 1542-1552.
29. Robert D., Rohr F., Weber J.V., *CR Acad. Sci.*, 325 (1997) 733-738.
30. Fotiadis C., Xekoukoulotakis N.P., Mantzavinos D., *Catalysis Today*, 124 (2007) 247-253.
31. Ali O., Namane A., Hellal A., *J. Ind. Eng. Chem.*, 19 (2013) 1384-1390.

(2017) ; <http://www.jmaterenvironsci.com>